A SURVEY OF DISLODGEABLE ORGANOPHOSPHATE RESIDUES ON SELECTED CROPS IN SAN LUIS OBISPO, SANTA BARBARA, AND VENTURA COUNTIES AT THE TIME OF HARVEST - 1984

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SUMMARY

In October 1984, foliage samples were collected during the harvest of 18 fields in San Luis Obispo, Santa Barbara, and Ventura Counties. These samples were analyzed for dislodgeable organophosphate pesticide residues using standard chromatographic techniques. Seventeen of the samples showed no detectable residues. The one positive sample was 100 times lower than the level currently considered safe at which to enter a field. These survey results indicate that there is compliance with existing worker safety intervals in the fields sampled.

INTRODUCTION

Field workers working in hand-harvested and/or manual labor intensive crops are considered to be one of the groups at greatest risk of being exposed to potentially hazardous pesticide residues. Periodic surveys are conducted to ensure that hazardous residue levels do not exist. Such surveys also serve to assess the effectiveness of reentry intervals, and may aid in identifying pesticides which require reevaluation of chemical degradation data.

METHODS

Three adjoining coastal counties were selected for this survey: San Luis Obispo, Santa Barbara, and Ventura. These three counties are responsible for producing a significant portion of the fresh hand picked vegetables grown in California. A number of crops are grown in this area, and harvest crews can be found working in this area nearly year round. During the time of this study, the majority of fields being harvested were broccoli and lettuce fields.

Foliage samples were randomly collected in fields where workers were present. A single sample consisting of 40 to 45 leaf disks was collected along a diagonal in each field. Samples were collected using a one-inch leaf punch (O. J. Birkestrand and Company, South El Monte, California). Replicate samples were not collected. Samples were collected in glass jars sealed with aluminum foil. They were stored and shipped on wet ice to the Worker Health and Safety Laboratory in Sacramento for analysis of organophosphate pesticides. Analytical procedures, minimum detectable quantities, and a list of pesticides detectable by the screening method are listed in the Appendix.

RESULTS AND DISCUSSION

A summary of survey results is given by crop in Table I. Eighteen samples were randomly collected from different fields. Only one of the 18 samples was found to contain an organophosphate pesticide. This sample was collected from a tomato field and contained 0.015 ug Diazinon/cm^2 of leaf surface. This level is approximately 250 times lower than the current estimated safe level for Diazinon (Maddy, 1985). At the estimated safe level, an unprotected worker may enter a field to conduct work involving substantial foliage contact and should not experience any acute or chronic illness symptoms. A recent report on the breakdown of Diazinon in the field, suggests that, at the level found in this tomato field, the application may have taken place three days prior to the harvest (Maddy, 1984b). This is highly likely, since worker safety regulations require at least one day to elapse before a worker may enter a tomato field after a Diazinon application and the label states that the application be made no less than one day before harvest.

The organophosphate pesticide residue levels found do not appear to be significant and there is no indication that reentry intervals required by regulation in California are inadequate to protect harvest workers. While the relatively small number of fields sampled cannot be considered representative of all fields in the study area, the results are consistent with

those of other studies conducted in previous years.

TABLE I

Results of 1984 Survey of Pesticide
Residues in Fields Being Harvested by Crop

	Pole Tomatoes	Green Beans	Lettuce	Broccoli	Celery
Total Fields Sampled	1	1	6	6	4
Number Positive	1	0	0	0	0

APPENDIX

ANALYTICAL PROCEDURES

The Screening of Dislodgable Pesticide Residues

SCOPE: This method is for the screening of dislodgeable organophosphate and chlorinated hydrocarbon residues on vegetation.

PRINCIPLE: Most organophosphate and chlorinated hydrocarbon pesticides are very soluble in ethyl acetate; therefore, this solvent is used to extract the pesticide. The analysis is by gas chromatography with NP and electron capture detectors.

REAGENTS AND EQUIPMENT:

(1) Sur-ten
(2) Ethyl acetate, nanograde
(3) Sodium sulfate anhydrous
(4) Rotary evaporator
(5) Rotator
(6) Various glassware
(7) Gas chromatograph with NP and electron capture detector

ANALYSIS: About 75 ml of water and four drops of 2% Sur-ten are added to the bottle containing the sample. The bottle is rotated for an hour. Decant off the water. This is repeated twice with two drops of Sur-ten and 50 ml water each. To the combined amount of water in a separatory funnel 75 ml ethyl acetate is added. The funnel is shaken gently for two minutes. The ethyl acetate is allowed to run through 50 g of sodium sulfate anhydrous. The water is extracted two more times with 50 ml of ethyl acetate each. The combined solvent is evaporated to dryness and redissolved in 5 ml of ethyl acetate. This is ready for organophosphate analysis with the NP detector. After screening for organophosphate, a small amount of attaclay is added to the solution and the sample well shaken. When it becomes clear, the ethyl acetate extract is introduced into the gas chromatograph with electron capture detector for chlorinated hydrocarbon determination.

Gas chromatograph condition:

Column: (1) 6 ft. 4% OV-101
(2) 6 ft. 50/50 mixture of 4% OV-101 and 6% OV-210
Oven: 170°C and 230°C
Injector: 250°C
Detector: 350°C
Gas flow: 30 ml/min

CALCULATIONS:

$$\frac{\text{ug}}{\text{sq cm}} = \frac{(\text{ng std})\ (\text{peak ht sample})\ (\text{final vol ml})}{(\text{peak ht std})\ (\text{ul injected})\ (\text{total area sq cm})}$$

$$\text{Total area} = (2N)\ (3.14)\ (r)\ (r)$$

Where N = number of disc in sample
r = radius of disc in cm

DISCUSSION: Sensitivity: 0.0001 ug/sq cm in parathion
0.0001 ug/sq cm in aldrin

REFERENCE: Zweig, Vol. VI, p. 132, p. 191.

PESTICIDE ACTIVE INGREDIENTS DETECTABLE BY ORGANOPHOSPHATE SCREEN

Pesticide

Azinphos-methyl (Guthion)
Carbophenothion (Trithion)
Chlorfenvinphos (Supona)
Chlorpyrifos (Dursban)
Coumaphos (Co-Ral)
Crotoxyphos (Ciodrin)
Demeton (Systox)
DDVP
Dialifor (Torak)
Diazinon
Dicrotophos (Bidrin)
Dimethoate (Cygon)
Dioxathion (Delnav)
Disulfoton (Disyston)
EPN
Ethion
Ethoprop (Mocap)
Fenamiphos (Nemacur)
Fenitrothion (Sumithion)
Fensulfothion (Dasanit)
Fenthion (Baytex)
Fonophos (Dyfonate)
Isofenphos (Oftanol)
Malathion
Methamidophos (Monitor)
Methidathion (Supracide)
Mevinphos (Phosdrin)
Naled (Dibrom)
Oxydemeton-methyl (Metasystox-R)
Parathion-ethyl
Parathion-methyl
Phorate (Thimet)
Phosalone (Zolone)
Phosmet (Imidan)
Phosphamidon (Dimecron)
Profenofos (Curacron)
Propetamphos (Safrotin)
Ronnel
Schradan (OMPA)
Sulprofos (Bolstar)
Tetrachlorvinphos (Gardona)
Thionazin (Zinophos)
Triazophos (Hostathion)

Other Chemicals Also Detected Using a Nitrogen-Phosphorus Detector

Molinate (Ordram)
Thiobencarb (Bolero)

Sensitivity

The Minimum Detectable Level (MDL) for each of these chemicals is at least 0.1 ug/cm^2 of leaf surface except for azinphos-methyl (Guthion) (2.5 ug/cm^2)* and phosalone (Zolone) (1 ug/cm^2). A more sensitive MDL may be obtained depending on the specific chemical and sample matrix.

* This is above the safe level of 1.6 ug/cm^2. The following is a list of the crops sampled and the percentage of the total acreage treated with azinphos-methyl with the number of applications in parenthesis:

Beans	0.03% (2)
Broccoli	0.8% (48)
Celery	3.3% (18)
Lettuce	0 (0)
Tomatoes	3.0% (169)

Thus, with the exception of celery and tomatoes, it would appear unlikely that workers would be exposed to hazardous levels of azinphos-methyl. Data from a dislodgeable residue study on pole tomatoes indicates that at

normal application rates, residue levels never exceed the safe level (1.6 ug/cm^2). Since applications rates for azinphos-methyl on celery are equal to or less than those for tomatoes, we would not expect levels on celery to exceed the safe level.

REFERENCES

1. Maddy, K. T.: Estimated Safe Levels of Foliar Residues on Crops to Allow Unprotected Workers Reentry into Treated Fields in California. California Department of Food and Agriculture. Worker Health and Safety Unit. HS-1280. 1985.

2. Maddy, K. T., S. L. Kilgore, C. R. Smith, and C. Cooper: Degradation of Dislodgeable Diazinon Residue on Chinese Cabbage and Broccoli Foliage in Santa Barbara and San Luis Obispo Counties. California Department of Food and Agriculture. Worker Health and Safety Unit. HS-1273. 1984b.